Chapter 7

Chlorophyll as Photosensitizer in Dye-Sensitized Solar Cells

Abdul Kariem Arof and Teo Li Ping

Additional information is available at the end of the chapter

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Abstract

Chlorophyll, being the most abundant pigment that commonly found in plants, bacteria, bryophytes and algae, plays a vital role in photosynthesis. Chlorophylls are natural pigments and therefore safe, environmental friendly, easily available and cheap. Chlorophyll has been experimented to function as a photosensitizer in dye-sensitized solar cells (DSSCs) as DSSCs mimic the photosynthesis process in green plants. DSSC was first developed by Gratzel in 1991 and since then has gained tremendous attention as its fabrication is cheap and easy. A DSSC basically comprises a semiconductor that has been soaked in sensitizing dye (chlorophyll), a counter electrode, and an electrolyte containing a redox mediator. The dye absorbs light, which is transformed into electricity. Chlorophyll can be extracted from the leaves of pomegranate, bougainvillea, papaya, *Pandanus amaryllifolius*, spinach, green grasses, seaweeds, algae and bryophytes. Chlorophyll from these sources has been studied as possible photosensitizers for DSSCs. Most researches done in chlorophyll DSSC use the extracted natural pigments. The type of solvent and pH of the dye solution will also affect the stability of chlorophyll and subsequently the performance of the DSSCs. This chapter will present an inexhaustive overview on DSSCs using chlorophyll as dye.

Keywords: chlorophyll, photosensitizer, light adsorption, dye-sensitized solar cells, efficiency

1. Introduction

Over billions of years, Mother Nature has been converting light from the sun into energy via photosynthesis. Sunlight is the most abundant and sustainable energy source that is free.

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The Earth receives energy from the sun at the rate of ~12×10^{17} J s^{-1} [1]. This has exceeded the yearly worldwide energy consumption rate of ~1.5×10^{13} J s^{-1} [1]. Therefore, it is a challenge to devise an approach for the effective capture and storage of solar energy for our consumption since fossil fuels such as oil and gas will be depleted in the years to come. In order to imitate the photosynthesis process, Gratzel and coworkers have developed dye-sensitized solar cells (DSSCs) based on the similar working mechanism [2]. Nevertheless, one main difference between photosynthesis of plants and DSSCs is that the energy can be stored in plants for later use but DSSC is unable to store energy. Ever since the birth of DSSCs, they have become the spotlight of attention among scientists and researchers around the world as they are much cheaper, easier to fabricate, and more environmental friendly when compared with conventional silicon solar cells [3, 4]. A DSSC is an electrochemical device that comprises a transparent-conducting oxide (TCO) glass over which is deposited a semiconductor. The semiconductor will be soaked in a dye solution. An electrolyte with reduction-oxidation (redox) mediator and cathode are the other remaining components. The fluorine-doped tin oxide (FTO)/semiconductor/dye assembly is referred to as photoanode. Indium-doped tin oxide (ITO) and FTO are two TCOs used commonly in DSSCs. Titanium dioxide (TiO_2) is one of the popular semiconductors used for DSSC since it is cheap, non-toxic, and possesses a large bandgap [5]. TiO_2 is deposited on the TCO substrate in the form of TiO_2 nanoporous particle network to increase the coverage area for the sensitizing dye. The cathode is made up of another TCO on top of which platinum is deposited. Carbon and conducting polymers can also be employed as counter electrode. If a gel polymer electrolyte is used, it is sandwiched between the photoanode and cathode. The dye, on the other hand, can be categorized into two groups: synthetic and natural. The most frequently used synthetic dye is the ruthenium (Ru)-based dyes but they are not environmental friendly since Ru is a heavy metal [6]. Such dyes are also very expensive due to the scarcity of Ru. By contrast, natural dyes are readily available and thus cheap besides being non-toxic, environmental friendly, biodegradable, easily extracted as well as can be used without any purification [6]. Since DSSC mimics the photosynthesis of green plants, therefore chlorophyll can also function as photosensitizer for DSSC. In fact, report on chlorophyll as photosensitizer on zinc oxide (ZnO) semiconductor was first published by Tributsch in 1972 [7].

2. Basic working principle of chlorophyll-sensitized DSSC

In this chapter, discussion is based on the TiO_2 semiconductor photoanode. However, occasionally we refer to zinc oxide (ZnO) and tin dioxide (SnO_2). The dye is chlorophyll extracted from various sources including leaves, grasses, flowers, seaweeds, and algae. The electrolyte is generally in the form of liquid and quasi-solid state. The commonly used mediator is the I^-/I_3^- redox couple and the counter electrode chosen in the preceding discussion is platinum (Pt) or carbon (C). Upon shining light on the cell, the molecules of the chlorophyll dye (D) will be excited (D^*) after absorbing photons ($h\nu$) and inject electrons into the semiconductor conduction band as described in the equation below:

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$$hv + D \rightarrow D^* \tag{1}$$

The excited chlorophyll molecules (D^*) will inject electrons into the TiO_2 conduction band and the excited dye will then be oxidized or ionized (D^+). The reaction process involved is as follows:

$$D^* + TiO_2 \rightarrow D^+ + e^-_{cb}(TiO_2) \tag{2}$$

The oxidized chlorophyll dye molecules (D^+) will accept electrons from an iodide ion (I^-) in the electrolyte when the I^- ions were released to the oxidized molecules and in turn oxidized to triiodide ions (I_3^-) according to the equation below:

$$2D^+ + 3I^- \rightarrow I_3^- + 2D \tag{3}$$

The electron in the TiO_2 conduction band flows out of the device through the load to reach the counterelectrode and reduced the triiodide ion as follows:

$$I_3^- + 2e^- \rightarrow 3I^- \tag{4}$$

The iodide ion is now restored, the electron circuit is completed, and the whole system is back to its original state to start a new cycle. These processes will continue as long as there is light and current is produced in the external circuit continuously. Under illumination, the voltage generated is given by the energy difference between the photoanode's Fermi level and the electrolyte's redox potential. **Figure 1** illustrates the schematic diagram of the chlorophyll-sensitized DSSC and its operating principle.

The light to electricity conversion efficiency (η) of the chlorophyll DSSC can be calculated from the equation below:

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \times 100\% \tag{5}$$

Here J_{sc} is the short circuit current density (unit: mA cm^{-2}), which is obtained without any external applied voltage or potential, V_{oc} is the open circuit voltage (unit: mV) obtained under the condition of open circuit when there is no current, P_{in} is the input power (total incident light power density), and FF is the fill factor which can be expressed as

$$FF = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}} \tag{6}$$

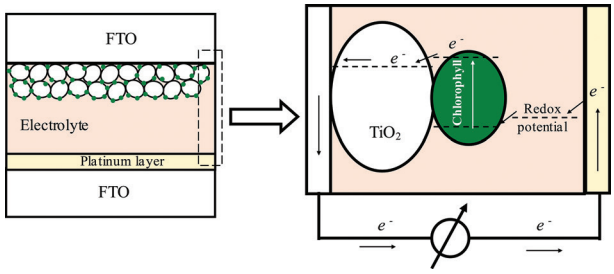


Figure 1. Operating principle of a chlorophyll-sensitized DSSC.

Here J_{max} and V_{max} are the photocurrent density and voltage in the *J-V* curve at the maximum power output. Each single component in a DSSC is important to ensure good performance. The main focus in this chapter is the chlorophyll dye. The dye is to absorb light, injects electrons into the semiconductor, and receives electrons from the redox mediator in the electrolyte. The cycle continues. An efficient dye sensitizer should display unique characteristics as listed below [8, 9]:

- Absorb light in the visible region.
- Good attachment at the surface of photoelectrode to ensure fast electron transfer.
- Good interfacial properties and high stability to enable good absorption to TiO_2.
- Easily accepting replacement electron from electrolyte.
- Excited state of dye must be slightly above the TiO_2 conduction band and its ground-state level below the redox potential of the electrolyte.
- Lifetime of the dye must be consistent with device life.
- Stable enough to sustain about 20 years exposure to natural light.

3. Performance of chlorophyll-sensitized DSSCs

Table 1 summarizes the performance of some DSSCs employing chlorophyll as photosensitizer reported by researchers worldwide. Herein, the illumination of the chlorophyll-sensitized DSSCs was carried out under intensity of 100 mW cm^{-2} unless stated otherwise.

It is evident that the condition of leaves whether fresh or dried affects the adsorption of chlorophyll onto the photoanode surface and consequently the performance. Taya et al. [10] observed that DSSCs having chlorophyll extracted from fresh leaves of *Anethum graveolens* (Indian traditional medicinal herb and spice) and arugula (arugula salad leaves) exhibited better performance than DSSCs with *A. graveolens* and arugula leaves that have been dried for 1 week. On the other hand, higher efficiencies were detected in DSSCs with dried parsley, spinach, and green algae as compared to fresh ones. However, the authors did not discuss the reason behind this. Among parsley, arugula, *A. graveolens*, *Spinach oleracea*, and green algae, chlorophyll extracted from spinach produced the best efficiency of 0.290 % [10]. The efficiency of the DSSCs depends on the soaking temperature and time. The 0.290% efficiency was obtained when the TiO_2 photoanode was soaked in the spinach extract solution at 60°C for 12 h [10]. Decreasing the temperature yielded low efficiency with η = ~0.0380% at 30°C. Beyond the optimum temperature, the efficiency decreased to ~0.175% (70°C) and ~0.0190% (80°C), respectively. Reducing the TiO_2 soaking time in the chlorophyll spinach solution to 2 h gave poor efficiency of ~0.021% [10]. Beyond 12 h of soaking, no obvious change in efficiency was observed from the spinach chlorophyll-sensitized DSSC [10]. Therefore, it can be inferred that the freshness of chlorophyll leaves, the soaking temperature of TiO_2 in chlorophyll solution, and its duration influenced the DSSC performance. From **Table 1**, comparison has been

Dye	Photoanode	Electrolyte	Counter electrode	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF*	η (%)	Ref.
Anethum graveolens leaves (fresh)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.965	0.579	0.400	0.220	[10]
Anethum graveolens leaves (dried)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.454	0.562	0.320	0.080	[10]
Arugula leaves (fresh)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.788	0.599	0.420	0.200	[10]
Arugula leaves (dried)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.713	0.594	0.430	0.180	[10]
Parsley leaves (fresh)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.535	0.445	0.340	0.070	[10]
Parsley leaves (dried)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.448	0.553	0.400	0.090	[10]
Bougainvillea spectabilis flower	TiO_2/ITO	I^-/I_3^- GPE	PEDOT/FTO	1.110	0.500	0.586	0.325	[11]
Amaranthus caudatus flower	TiO_2/ITO	I^-/I_3^- GPE	PEDOT/FTO	1.820	0.550	0.610	0.610	[11]
Cordyline fruticosa leaves	TiO_2	Not stated	Not stated	1.300	0.616	0.602	0.500	[12]
Pawpaw leaves	TiO_2/FTO	LE	Not stated	0.649	0.504	0.605	0.200	[13]
Pomegranate leaves	TiO_2/ITO	I^-/I_3^- LE	Pt/FTO	2.050	0.560	0.520	0.597	[14]
Platanus orientalis L. (Chinar leaves)	TiO_2/ITO	I^-/I_3^- LE	Pt/ITO	0.012	0.468	0.004	0.550	[15]
Shiso leaves	TiO_2/FTO	p-CuI	-	3.520	0.432	0.390	0.590	[16]
Bougainvillea leaves	Au/TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	3.230	0.500	0.410	0.618	[17]
Ocimum Gratissimum (scent leaves)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.044	0.466	0.400	0.021	[18]
Spinach oleracea	TiO_2/ITO	I^-/I_3^- LE	Pt/ITO	0.467	0.550	0.510	0.131	[19]
Spinach oleracea (fresh)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.332	0.590	0.420	0.080	[10]
Spinach oleracea (dried)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	1.110	0.583	0.460	0.290	[10]
	ZnO/FTO	I^-/I_3^- LE	Pt/FTO	0.123	0.226	0.200	0.008	[10]
Red spinach leaves	TiO_2/ITO	I^-/I_3^- LE	C/FTO	1.000	0.505	0.578	0.583	[20]
	TiO_2/ITO	I^-/I_3^- LE	C/FTO	0.700	0.559	0.455	0.357	[20]
	TiO_2/ITO	I^-/I_3^- LE	C/FTO	0.500	0.750	0.394	0.296	[20]
Green spinach leaves	ZnO/ITO	I^-/I_3^- LE	C/ITO	0.052	0.590	0.530	0.016	[21]

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Dye	Photoanode	Electrolyte	Counter electrode	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF*	η (%)	Ref.
Papaya leaves	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.360	0.325	0.560	0.070	[22]
	TiO_2/ITO	I^-/I_3^- LE	C/FTO	0.060 mA	0.394	0.250	-	[23]
Jatropha leaves	TiO_2/ITO	I^-/I_3^- LE	C/FTO	0.042 mA	0.350	0.250	-	[23]
Ipomoea leaves extract	TiO_2/ITO	I^-/I_3^- LE	Pt/ITO	0.850	0.495	0.536	0.233	[19]
	TiO_2/ITO	I^-/I_3^- LE	Pt/ITO	0.914	0.540	0.563	0.278	[19]
	TiO_2/ITO	I^-/I_3^- LE	Pt/ITO	0.825	0.533	0.548	0.259	[19]
	TiO_2/ITO	I^-/I_3^- LE	Pt/ITO	1.120	0.565	0.592	0.318	[19]
	TiO_2/ITO	I^-/I_3^- LE	Pt/ITO	0.982	0.543	0.564	0.292	[19]
	TiO_2/ITO	I^-/I_3^- LE	Pt/ITO	0.915	0.510	0.552	0.253	[19]
Azadirachta indica (Neem) leaves	TiO_2/FTO	I^-/I_3^- LE	C/FTO	0.430	0.404	0.401	0.720	[24]
	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.230	0.467	0.392	0.050	[25]
Ziziphus jujuba leaves (dried)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	3.180	0.652	0.519	1.077	[26]
Basil leaves (dried)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	1.398	0.581	0.499	0.409	[26]
Basil flower	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	1.120	0.600	0.400	0.270	[27]
Mint flower	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.450	0.560	0.380	0.090	[27]
Mint leaves (dried)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.980	0.579	0.400	0.227	[26]
Lemon leaves[a]	TiO_2/FTO	I^-/I_3^- LE	C/FTO	1.080	0.592	0.100	0.036	[28]
Morula leaves[a]	TiO_2/FTO	I^-/I_3^- LE	C/FTO	0.059	0.472	0.050	0.001	[28]
Fig leaves (dried)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	2.091	0.596	0.515	0.642	[26]
Berry leaves (dried)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	3.573	0.595	0.441	0.939	[26]
Pandanus amaryllifolius leaves	TiO_2/ITO	GPE	Pt/ITO	1.610	0.360	0.410	0.240	[29]
	TiO_2/FTO	GPE	Pt/FTO	1.190	0.490	0.630	0.390	[30]
	TiO_2/FTO	GPE	Pt/FTO	1.910	0.480	0.560	0.510	[31]

Dye	Photoanode	Electrolyte	Counter electrode	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF*	η (%)	Ref.
Banana leaves (dried)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	1.770	0.596	0.492	0.522	[26]
Peach leaves (dried)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	2.555	0.611	0.422	0.659	[26]
Black tea leaves	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.390	0.550	0.400	0.080	[27]
Coccinia indica leaves	SnO_2/FTO	I^-/I_3^- LE	Not stated	0.700	0.540	0.610	0.260	[32]
	La-SnO_2/FTO	I^-/I_3^- LE	Not stated	0.820	0.540	0.540	0.290	[32]
	La-Cu-SnO_2/FTO	I^-/I_3^- LE	Not stated	1.010	0.560	0.510	0.310	[32]
Ficus retusa Linn.	Au-TiO_2/ITO	$Ce^{4+/3+}$ LE	Pt/ITO	7.850	0.520	0.289	1.180	[33]
Garcinia suubelliptica	Au-TiO_2/ITO	$Ce^{4+/3+}$ LE	Pt/ITO	6.480	0.322	0.331	0.691	[33]
Perilla	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	1.360	0.522	0.696	0.500	[34]
Petunia	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.850	0.616	0.605	0.320	[34]
Eggplant pulp	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.350	0.630	0.390	0.090	[27]
Festuca ovina grass	TiO_2/ITO	I^-/I_3^- LE	C/ITO	1.189	0.548	0.699	0.460	[35]
Hierochloe odorata grass	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	2.199	0.594	0.355	0.460	[36]
Torulinium odoratum grass	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	1.004	0.654	0.483	0.320	[36]
Dactyloctenium aegyptium grass	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.698	0.719	0.481	0.240	[36]
Moss bryophyte *(hyophila involuta)*	TiO_2/FTO	GPE	Pt/FTO	5.780	0.600	0.570	1.970	[37]
	TiO_2/FTO	GPE	Pt/FTO	4.590	0.610	0.640	1.770	[38]
	TiO_2/FTO	GPE	Pt/FTO	5.960	0.580	0.580	2.000	[38]
	TiO_2/FTO	GPE	Pt/FTO	3.710	0.640	0.720	1.690	[38]
	TiO_2/FTO	GPE	Pt/FTO	5.370	0.550	0.730	2.170	[38]
	TiO_2/FTO	GPE	Pt/FTO	8.440	0.540	0.580	2.620	[38]
Rhoeo spathacea (Sw.) Stearn	Au-TiO_2/ITO	$Ce^{4+/3+}$ LE	Pt/ITO	10.900	0.496	0.274	1.490	[33]
Sargassum wightii (marine seaweed)[b]	ZnO/FTO	I^-/I_3^- LE	Pt/FTO	0.203	0.330	0.460	0.070	[39]

Dye	Photoanode	Electrolyte	Counter electrode	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF*	η (%)	Ref.
Kelp (brown algae)	TiO_2/TCO	I^-/I_3^- LE	Pt/TCO	0.433	0.441	0.620	-	[40]
Undaria pinnatifida (brown seaweed)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.800	0.360	0.690	0.178	[41]
	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	10.700	0.530	0.600	3.400	[42]
	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	13.800	0.570	0.580	4.600	[42]
	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	8.600	0.470	0.600	2.500	[42]
	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	9.000	0.470	0.610	2.600	[42]
Cladophora sp. (green algae)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.145	0.585	0.590	0.055	[43]
Green algae (fresh)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.134	0.416	0.210	0.010	[10]
Green algae (dried)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	0.397	0.559	0.440	0.100	[10]
Chlorella vulgaris (microalgae)	TiO_2/FTO	I^-/I_3^- LE	Pt/FTO	2.530	0.551	0.650	0.900	[44]

[a]Intensity 80 mW cm^{-2}.

[b]Intensity 45 mW cm^{-2}.

LE: liquid electrolyte; GPE: gel polymer electrolyte; PEDOT: poly(3,4-ethylenedioxythiophene).

Table 1. The photovoltaic performance of some chlorophyll-sensitized DSSCs.

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made between TiO_2 and ZnO photoanodes for chlorophyll spinach DSSCs where the former gave better performance than the latter [10].

In the case of chlorophyll extract from ipomoea leaves (leaves of morning glory flower), 50°C is the optimum temperature for TiO_2 immersion with efficiency of 0.278% [19]. Lower efficiencies of 0.233 and 0.259% were obtained when the TiO_2-soaking temperature in ipomoea leaves extract solution were at 30 and 80°C, respectively for 24 h [19]. Other than temperature, pH of the dye solution is another factor influencing the efficiency. Maintaining the soaking temperature at 50°C, the pH of ipomoea dye solutions was adjusted to pH 1, 2, and 3 [19]. However, there was no mention on the type of acid used. Thus, it is not known whether the anion of acid had any influence on the DSSC performance. Nevertheless, improvement in efficiency can be seen when the acidity of the dye solution was adjusted to pH 1 and 2 with efficiencies of 0.318 and 0.292%, respectively. However, further increasing the pH to 3 decreased the efficiency (η = 0.253%) [19].

The type of solvent used for pigments extraction can also give different results in the absorption spectrum [45–47]. From the work of Al-Alwani et al. [45], it has been reported that the UV-vis absorption spectra of chlorophyll extracted from *Pandanus amaryllifolius* (screwpine leaves) and *Cordyline fruticosa* (commonly known as Ti plant or cabbage palm) in ethanol and methanol solution displayed highest intensity absorption peaks among other solvents such as n-butyl alcohol, ethyl-acetate, n-hexane, chloroform, acetonitrile, ethyl-ether, and petroleum ether. Then, 1 g TiO_2 powder was added in chlorophyll extracted from *P. amaryllifolius* and *C. fruticosa* in respective solvents (ethanol for Pandanus leaves and methanol for *Cordyline* leaves) and water at different ratios. The addition of an appropriate quantity of water into the respective alcohol solvent increased the polarity of solution for better dye adsorption on the TiO_2 surface [45]. For solution containing TiO_2 and *P. amaryllifolius* chlorophyll, the best absorption spectrum was obtained at 2:1 of ethanol to water ratio, whereas the optimum ratio for TiO_2-*C. fruticosa* solution with mixture solvents of methanol and water was 3:1. Better dye absorption onto TiO_2 surface is said to improve the performance of DSSCs but there is no DSSC results in Ref. [45]. Nonetheless, in recent publication [12], the same group of authors have turned to response surface methodology (RSM) approach to investigate the various parameters involved in the chlorophyll extraction process from *C. fruticosa* simultaneously and then predict their response in order to obtain the optimized condition for its extraction. After taking three factors into consideration, that is, boiling temperature for organic solvents (acetonitrile, ethanol, and methanol), different pH ranging from 4 to 8 and temperature for chlorophyll extraction from 50 to 90°C, it was found that chlorophyll can be best extracted from the cordyline leaves under the condition where the solvent was ethanol (boiling point 78°C), pH of 7.99, and at temperature of 78.33°C [12]. As a result, the efficiency of 0.500% was obtained for DSSC with *C. fruticosa* chlorophyll as listed in **Table 1**.

It should be noted that both betalain and chlorophyll pigments can be extracted from the flowers of *Amaranthus caudatus* (common name: love-lies-bleeding, velvet flower) and *Bougainvillea spectabilis* using different solvents. Chlorophyll pigments have been obtained when 0.1 mol L^{-1} hydrochloric acid (HCl) was used to dissolve the amaranthus and bougainvillea flowers, whereas ethanol as solvent will yield betalain pigments from the same flowers. Surprisingly,

DSSCs having chlorophyll from amaranthus and bougainvillea flowers in **Table 1** demonstrated better performance as compared to DSSCs with betalain from the same flowers. The J_{sc}, V_{oc}, *FF*, and η values of betalain DSSC from *B. spectabilis* were 0.081 mA cm^{-2}, 0.450 V, 0.483, and 0.018%, respectively [11]. DSSCs using betalain extracted from *A. caudatus* flower gave the J_{sc} of 0.102 mA cm^{-2}, V_{oc} of 0.530 V, *FF* of 0.610, and η of 0.033% [11]. The efficiencies exhibited by chlorophyll-sensitized DSSCs from amaranthus (η = 0.610 %) and bougainvillea (η = 0. 325 %) flowers were surprisingly high considering that gel polymer electrolyte and PEDOT counter-electrode were used instead of conventional liquid electrolyte and Pt electrode [11].

Khan and coworkers [20] have examined the effect of acid treatment on TiO_2 nanoparticles in the making of TiO_2 paste to be coated on ITO glass substrate via the doctor blade method. It is found that chlorophyll from red spinach leaves-sensitized DSSC without any acid treatment on TiO_2 photoanode exhibited the efficiency of 0.296% which is lower than the TiO_2 acid-treated DSSC with chlorophyll extracted from the same source under intensity of 50 mW cm^{-2} [20]. The presence of acid can prevent agglomeration of TiO_2 nanoparticles and results in better TiO_2 dispersion and thereby offer more adsorption sites for the dye molecules [20]. Khan et al. [20] used citric acid (organic acid) and nitric acid (inorganic acid) to prevent TiO_2 agglomeration in the DSSC fabricated with chlorophyll from red spinach leaves, and TiO_2 treated with citric acid gave higher efficiency of 0.583% compared to that using nitric acid treatment on TiO_2 electrode (η = 0.357%). The lower efficiency yielded by nitric acid treatment could be due to nitric acid being a strong oxidizing acid and its corrosive nature may ruin the TiO_2 surface [48]. From **Table 1**, the J_{sc} and *FF* of the DSSC with chlorophyll extracted from red spinach leaves can also be seen to increase with efficiency following the order η (TiO_2) < η (nitric acid treated TiO_2) < η (citric acid treated TiO_2), whereas the V_{oc} values decreased in the same order.

It can be noted from **Table 1** that SnO_2 was employed as photoanode instead of TiO_2 in the cell having chlorophyll extracted from *Coccinia indica* (ivy gourd) leaves [32]. Comparison with TiO_2 revealed that SnO_2 is chemically stable and has larger bandgap of 3.6 eV and higher electron mobility [49, 50]. Due to its wide bandgap, it is less sensitive to UV degradation and thus possesses better stability as compared to TiO_2 [51]. Nonetheless, its large bandgap will also cause SnO_2 to have lower open circuit voltage. SnO_2 having high electron mobility can yield fast electron transport and therefore electron recombination can be decreased. From the table, the cells with chlorophyll from *C. indica* leaves exhibited the efficiencies of 0.260, 0.290, and 0.310% using three photoanodes, that is, SnO_2, La-doped SnO_2, and La-Cu-doped SnO_2, respectively [32]. Doping elements into DSSC photoanode improved the performance since more dye molecules can be adsorbed in the working electrode due to larger surface area owing to increased roughness and pores after doping [52].

Chang et al. [17] have investigated the plasmonic effect of gold (Au) nanoparticles with an average size of 27 nm in TiO_2 DSSC using chlorophyll from bougainvillea leaves. An efficiency of 0.618% was obtained. The Au nanoparticles showed localized surface plasmon resonance behavior when the frequency of the incident light came close to the surface plasmon frequency of Au and consequently improved light absorption leading to a considerably high efficiency of 0.618% as listed in **Table 1**. Also, the interface between Au and TiO_2 formed a Schottky barrier

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where electrons will be blocked from re-entering the dye or electrolyte, which decreased electron recombination and improved the DSSC performance. Earlier report on TiO_2 loaded with Au nanoparticles prior to chlorophyll sensitization was published by Lai and coworkers [33]. Instead of using I^-/I_3^- LE, the authors employed water-based electrolyte at ethanol:water ratio of 7:13 with $Ce^{4+/3+}$ as redox couple since water-based DSSC can be totally free from toxic and is biologically friendly. The chlorophyll was extracted from herbal plant *Rhoeo spathacea* (Sw.) Stearn. Unexpectedly, an efficiency of more than 1% was produced by the chlorophyll *R. spathacea* water-based DSSC which is higher than that of a similar cell but with one of the earliest synthetic dyes, that is, crystal violet ($\eta = 0.010\%$) [33]. The authors attributed the aggregation of crystal violet dyes as the culprit behind this based on its photocurrent density value (J_{sc} = 2.040 mA cm^{-2}), which is lower than that of *R. spathacea* cell (J_{sc} = 10.900 mA cm^{-2}) [33]. In fact, the other two water-based DSSCs using chlorophyll extracted from *Ficus retusa* Linn. (common name: bonsai plant) and *Garcinia subelliptica* (common name: happiness tree) have also demonstrated higher efficiency than that of crystal violet-sensitized DSSC with efficiencies of 1.180 and 0.691%, respectively [33].

From **Table 1**, it can be observed that most of the DSSCs employ liquid electrolytes based on I^-/I_3^- redox mediator. The maximum power conversion efficiencies of liquid electrolyte-based DSSCs using synthetic dyes have reached around 14% [53]. Liquid-based electrolytes are desired since they can infiltrate into the TiO_2 nanopores network to make contact with the dye molecules for dye regeneration. Still, liquid electrolyte-based cells have limited durability due to the possibility of leakage and volatility of solvents. Some of the solvents are flammable as well. In an attempt to avoid these complications, researchers worldwide are focusing on developing polymer-based electrolytes for DSSCs. Solid polymer electrolytes can exhibit reasonable ionic conductivities but have poor interfacial contact with electrodes. Hence, gel-type polymer electrolytes (GPEs) are being developed. GPEs, which are basically liquid electrolyte trapped in the polymer matrix, have good flexibility and conductivities comparable to those of liquid electrolytes. It can be clearly seen from **Table 1** that the DSSC using chlorophyll extracted from moss bryophyte and gel polymer electrolyte exhibited exceptionally high efficiencies of ~2–2.620% under different conditions. The bryophyte cell with η = 1.970% was obtained with GPE having polyacrylonitrile (PAN) as polymer host, tetrapropylammonium iodide (TPAI) salt, iodine, ethylene carbonate (EC), and propylene carbonate (PC) as solvent and plasticizer [37]. Efficiencies of 1.770 and 2.000% were attained for bryophyte cells using GPE based on poly(vinyl alcohol) (PVA) with single [potassium iodide (KI)] and double salts (KI and TPAI), respectively [38]. Higher efficiency and J_{sc} values observed in the cell having binary salts GPE could be most probably due to the higher number of iodide ions contained in the GPE. As for the second best performing chlorophyll bryophyte DSSC (η = 2.170 %), it is acquired using GPE based on poly(vinyl alcohol) (PVA) and double salts of potassium iodide (KI) and TPAI with the addition of 0.7 M tert-butylpyridine (TBP) [38]. TBP can be used either by incorporating it in electrolyte or photoanode in order to improve the V_{oc} and subsequently η. However, in this case where TBP was added into GPE, the TBP effect is insignificant as compared to the bryophyte cell when the working electrode was immersed in TBP for 1 h (η = 1.690%) [38]. Nonetheless, the efficiency of the latter is lower than the former owing to its lower J_{sc} value which might be due to lesser photon harvesting as a result of reflection

and light scattering by TBP [38]. The most efficient chlorophyll bryophyte DSSC having η of 2.620% was attained when a co-adsorbent, that is, chenodeoxycholic acid (CDCA), was added in the moss bryophyte [38]. The GPE used was PVA-based double salt without TBP. CDCA served as spacer to prevent the self-aggregation of chlorophyll molecules, diminish electron recombination, and stabilize the chlorophyll, thereby improving the efficiency.

It is worth mentioning from **Table 1** that the cell having the efficiency of 0.590% with chlorophyll extracted from shiso leaves used copper iodide (CuI) as hole transport material (HTM) instead of conventional liquid electrolyte [16]. Therefore, the DSSC has the configuration of FTO/TiO_2/chlorophyll dye/CuI. CuI, a p-type semiconductor, has bandgap of 3.1 eV and good optical transparency [54, 55]. The p-CuI was coated onto the chlorophyll/TiO_2/FTO using dip- and spray-coating technique as this method involves low calcination temperature and thus the degradation of dye will not occur [16, 54]. The p-CuI solid-state DSSC has similar working principle with conventional DSSC except that after photon absorption, the dye molecules will be excited and then inject electrons and holes into TiO_2 and p-CuI, respectively. This indicates that the dye at ground state must be positioned below CuI valence band and the dye-excited state should be above the TiO_2 conduction band in order to ensure proper functioning of chlorophyll CuI DSSC. With the usage of HTM, there will be no issue on pigment deterioration since natural pigment is unstable against the oxidized species in electrolyte with iodine as redox mediator [16].

Most of the reports on chlorophyll-sensitized DSSCs summarized in **Table 1** do not contain information on the type of chlorophyll used. Among the six chlorophylls, chlorophyll *a*, which plays vital role in photosynthesis process, shows poor adsorption and sensitization on TiO_2 due to its structure that contains phytyl and alkyl groups causing steric hindrance that obstruct the chlorophyll molecules to bind efficiently with TiO_2 molecules [40, 56, 57]. The structure of chlorophyll *b* only differs from chlorophyll *a* by the aldehyde group (–CHO) rather than methyl group (–CH_3). On the other hand, chlorophyll *c*, which consists of chlorophyll c_1 and chlorophyll c_2, has carboxyl group (–COOH) that can effectively attach to TiO_2 as reported in Ref. [41]. Chlorophyll *c*, which is the main pigment in *Undaria pinnatifida* (brown seaweed) yielded the efficiency of 0.178% when applied in DSSC as listed in **Table 1**. Wang et al. [42] have purified the pigments in *U. pinnatifida* to obtain chlorophyll *c* and remove chlorophyll *a* and carotenoids. Then, the purified chlorophyll *c* was subjected to polyethylene column chromatography to isolate chlorophyll c_1 and chlorophyll c_2. Using the same method, chlorophyll c_1 and chlorophyll c_2 in oxidized form can also be obtained. As a result, efficiencies of 3.400 and 4.600% have been obtained from the chlorophyll c_1 and chlorophyll c_2-sensitized DSSCs with liquid electrolyte [42]. Decrement in efficiency can be seen in DSSCs employing oxidized chlorophyll c_1 (designated as chlorophyll c'_1) and oxidized chlorophyll c_2 (chlorophyll c'_2) with the values of 2.500 and 2.600%, respectively [42]. Nonetheless, to the best of our knowledge, the chlorophyll-sensitized DSSC utilizing chlorophyll c_2 extracted from *U. pinnatifida* exhibited the highest efficiency among other chlorophyll-sensitized DSSCs till date. However, there remains the stability issue encountered by chlorophyll-sensitized DSSCs. Therefore, further work must be done to enhance the stability as well as improving the chlorophyll-sensitized DSSCs performance before they can be put into practical usage.

4. Summary

It has been shown that chlorophyll has good potential to serve as photosensitizer in dye-sensitized solar cells. Moreover, they are cheap, non-toxic, biodegradable, easily found, and easy to use as sensitizer. Although the efficiency is still considerably low with highest efficiency to date being only 4.600% from DSSC with *U. pinnatifida* chlorophyll c_2, there remains the possibility and room for improvement to further enhance the performance and improve stability of chlorophyll-sensitized DSSCs for practical applications.

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Author details

Abdul Kariem Arof* and Teo Li Ping

*Address all correspondence to: akarof@um.edu.my

Centre for Ionics University of Malaya, Physics Department, Faculty of Science, Kuala Lumpur, Malaysia

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